Soil, Plant, and Terrain Effects on Natural Perchlorate Distribution in a Desert Landscape

B. J. Andraski,* W. A. Jackson, T. L. Welborn, J. K. Böhlke, Ritesh Sevanthi, and D.A. Stonestrom

Perchlorate (ClO$_4^-$) is a contaminant that occurs naturally throughout the world, but little is known about its distribution and interactions in terrestrial ecosystems. The objectives of this Amargosa Desert, Nevada study were to determine (i) the local-scale distribution of shallow-soil (0–30 cm) ClO$_4^-$ with respect to shrub proximity (far and near) in three geomorphic settings (shoulder slope, footslope, and valley floor); (ii) the importance of soil, plant, and terrain variables on the hillslope-distribution of shallow-soil and creosote bush [Larrea tridentata (Sessé & Moc. ex DC.) Coville] ClO$_4^-$; and (iii) atmospheric (wet plus dry, including dust) deposition of ClO$_4^-$ in relation to soil and plant reservoirs and cycling. Soil ClO$_4^-$ ranged from 0.3 to 5.0 µg kg$^{-1}$. Within settings, valley floor ClO$_4^-$ was 17× less near shrubs due in part to enhanced leaching, whereas shoulder and footslope values were ~2× greater near shrubs. Hillslope regression models (soil, $R^2 = 0.42$; leaf, $R^2 = 0.74$) identified topographic and soil effects on ClO$_4^-$ deposition, transport, and cycling. Selective plant uptake, bioaccumulation, and soil enrichment were evidenced by leaf ClO$_4^-$ concentrations and Cl$^-$/ClO$_4^-$ molar ratios that were ~8000× greater and 40× less, respectively, than soil values. Atmospheric deposition ClO$_4^-$ flux was 343 mg ha$^{-1}$ yr$^{-1}$, ~10× that for published southwestern US wet-deposition fluxes. Creosote bush canopy ClO$_4^-$ (1310 mg ha$^{-1}$) was identified as a previously unrecognized but important and active reservoir. Nitrate $^{81}$O analyses of atmospheric deposition and soil supported the leaf-cycled–ClO$_4^-$ input hypothesis. This study provides basic data on ClO$_4^-$ distribution and cycling that are pertinent to the assessment of environmental impacts in desert ecosystems and broadly transferable to anthropogenically contaminated systems.

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**Abbreviations:** A, slope aspect; ADRS, Amargosa Desert Research Site; CV, coefficient of variation; DEM, digital elevation model; DW, distilled deionized water; F5, footslope; G, slope gradient; GEN, general curvature; PLAN, plan or across-slope curvature; PROF, profile or downslope curvature; SS, shoulder slope; TOC, total organic carbon; VF, valley floor; Z, elevation.

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Lycium pallidum in the environment (e.g., Rao et al., 2007). Perchlorate is highly water soluble and is repelled by soil particles’ negative surface charge, and it is therefore generally assumed to be highly mobile like Cl\(^-\) and NO\(_3\)^- with respect to soil–water transport and leaching. Perchlorate can persist in the environment due to the high activation energy required for reduction, but under anaerobic conditions it can be used as an electron acceptor by microbes and reduced to Cl\(^-\) and O\(_3\) (Coates and Achenbach, 2004). Limited soil leaching and enhanced aeration are two oft-cited factors promoting accumulation and persistence of natural ClO\(_4\)^- in semiarid–arid environments. Regarding anion gains and losses in the root zone, ClO\(_4\)^- is generally assumed to be less conservative than Cl\(^-\) because ClO\(_4\)^- may be lost due to microbial reduction and/or plant accumulation and to be more conservative than NO\(_3\)^- because NO\(_3\)^- is subject to preferential uptake, losses by denitrification and volatilization to gases, and gains by biological nitrogen fixation (Rao et al., 2007). Data pertaining to root-zone processes and plant uptake of ClO\(_4\)^- in natural settings are scarce. Existing ClO\(_4\)^- uptake and fate data largely were collected to characterize highly contaminated industrial sites, to assess phytoremediation strategies for such sites, and to evaluate agronomic plant ingestion risk to humans and livestock. Field studies have shown plant accumulation of ClO\(_4\)^- at industrial sites (e.g., Smith et al., 2004; Tan et al., 2004) and agricultural sites irrigated with ClO\(_4\)^-–bearing water (e.g., Jackson et al., 2005; Sanchez et al., 2005). Laboratory experiments have indicated little or no ClO\(_4\)^- reduction within plants (Van Aken and Schnoor, 2002; Seyfferth et al., 2008), and recent glasshouse studies have shown that agronomic plants selectively take up ClO\(_4\)^- under certain conditions (Ha et al., 2013). These results, in combination with the dominant control of vegetation on the overall soil–water balance, underscore the potential importance of plant-induced controls on the transport and fate of ClO\(_4\)^- in natural settings.

During the past decade, research has clearly demonstrated the worldwide occurrence of natural ClO\(_4\)^-, but little is known about its distribution and interactions in terrestrial ecosystems. Basic data are needed to improve understanding of controls and feedbacks on ClO\(_4\)^- in the soil–plant–atmosphere continuum and to assess risks associated with ecological health and potential mobilization of ClO\(_4\)^- to groundwater. In this paper we present results of a field study to determine the physical and biological factors affecting the distribution of natural ClO\(_4\)^- in a desert-shrub landscape. The study consisted of three major elements with complementary objectives: (i) to determine the local-scale distribution of shallow-soil (0–30 cm) ClO\(_4\)^- with respect to shrub proximity in three geomorphic settings (shoulder slope [SS], footslope [FS], and valley floor [VF]); (ii) to describe the relative importance of selected soil, plant, and terrain variables on the hillslope-scale distribution of ClO\(_4\)^- in shallow soil and creosote bush leaves; and (iii) to characterize the concentration and flux of ClO\(_4\)^- in atmospheric (wet plus dry, including dust) deposition and assess the magnitude of this direct atmospheric input with respect to the soil and plant reservoirs and cycling. In addition to the ClO\(_4\)^- data, soil physical properties, plant and terrain metrics, and other chemical and isotopic properties were determined to aid interpretation of the ClO\(_4\)^- distributions. A notable aspect of this study is the comprehensive range of data used to assess soil–plant–terrain–atmosphere interactions. The results of this study demonstrate the complexity of ClO\(_4\)^- distribution in a desert landscape and identify individual and combined factors that can influence distribution and cycling at the local and hillslope scales. Uncertainties are evaluated to identify knowledge gaps and areas of future research.

**Materials and Methods**

**Study Area**

Data collection was done at and in the vicinity of the USGS Amargosa Desert Research Site (ADRS), which is located in southwestern Nevada, 17 km south of Beatty and 20 km east of Death Valley National Park (Fig. 1). As part of the Mojave Desert ecosystem, the Amargosa Desert is one of the driest regions in the United States. Annual precipitation at the ADRS averaged 108 mm from 1981 to 2011 (Arthur et al., 2012). Vegetation is sparse, with total shrub-canopy ground cover ranging from about 5 to 10%. Shrubs include creosote bush, shadskle [or spiny saltbush, Atriplex confertifolia (Torr. & Frém.) S. Wats.], burrobush [or bursage, Ambrosia dumosa (Gray) Payne], wolfberry (Lycium pallidum Miers), and Mormon tea (Ephedra nevadensis S. Wats.). Surface soils in the study area belong to two associations: (i) Yermo (loamy-skeletal, mixed, superactive, calcareous, thermic Typic Torriorthents)—Arizo (sandy-skeletal, mixed, thermic Typic Torriorthents) and (ii) Commski (loamy-skeletal, carbonatic, thermic Typic Haplacalcids)—Yermo. Geologic mapping of the area identified surficial units ranging in age from Holocene to Plio-Pleistocene (Swadley and Parrish, 1988).

**Local-scale Distribution of Soil Perchlorate in Three Geomorphic Settings**

A feature-based sampling approach was used to establish local-scale distribution differences in shallow-soil (0–30 cm)
ClO$_4^-$ with respect to shrub proximity within and among three geomorphic settings. Additional soil chemical and physical properties (listed below) were determined to aid in interpretation of the ClO$_4^-$ results. The three distinct geomorphic settings were designated as SS, FS, and VF. General descriptions of surface characteristics for the sampling areas selected within each setting are given in Table 1. Two levels of shrub proximity—far (Far) and near (Near)—were defined by soil-sample distance to the nearest shrub or shrub clump (hereafter, shrub is used to refer to both shrub and shrub clump). The local-scale sampling areas selected within each geomorphic setting were restricted to avoid influential surface features (e.g., gullies) and to include soil-interspace areas large enough to collect Far samples at least 3 m from the center of the nearest shrub. The actual distances from shrub center to Near and Far soil-sample locations averaged 0.95 ± 0.31 m (SD unless otherwise noted) and 4.21 ± 1.27 m, respectively. The average shrub canopy radius associated with the sample locations was 0.68 m, giving normalized sample distances (distance divided by canopy radius) for Near and Far that averaged 1.4 and 6.2 times the canopy radius, respectively. Biotic influences on soil properties in desert–shrub interspace areas have been reported to extend to 1.34 (Caldwell et al., 2012) and 2 to 4 (Bedford and Small, 2008) times the canopy radius. Locations of the SS and FS sampling areas, which were on the same knoll, are shown in Fig. 2.

Soil samples for chemical and physical analyses were obtained by digging a pit and collecting a channel sample (~3.8 × 3.8 cm, 0- to 30-cm depth) from a vertical pit wall. Analyses included ClO$_4^-$, Cl$^-$, NO$_3^-$ as nitrogen (NO$_3^-$–N), total organic carbon (TOC), carbonate C (CO$_3^2$–C), and particle size (gravel, sand, silt, and clay). Soil ClO$_4^-$, Cl$^-$, and NO$_3^-$–N analyses were done at Texas Tech University. Solutés were extracted from soil samples (50 g) by adding distilled deionized water (DIW) at a 2:1 water-to-soil mass ratio and shaking for 24 h. Slurries were centrifuged for 20 min, after which the supernatant was filtered using a 0.2-μm nylon membrane ion-chromatography certified syringe filter. Following Rao et al. (2007), all extraction sets were accompanied by an extraction duplicate and extraction sample spike (soil + known amount of ClO$_4^-$ spike), extraction blank (DIW only), and extraction spike (known amount of ClO$_4^-$ in solution). Soil moisture content was determined by oven drying a subsample (105°C for 24 h). Perchlorate was quantified using an IC-MS/MS technique (Koester et al., 2000). The IC system (LC20, Dionex Corp.) consisted of a GP50 pump, a CD25 conductivity detector, an AS40 automated sampler, and an IonPac AS16A column (4 × 250 mm). Chloride and NO$_3^-$ were analyzed following USEPA Method 300.0 using a Dionex LC20, an IonPac AS14A column (4 × 250 mm), 8 mmol L$^{-1}$ Na$_2$CO$_3$–1 mmol L$^{-1}$ NaHCO$_3$ eluent, and an Anion Atlas electrolytic suppressor. The Cl$^-$ and NO$_3^-$–N reporting limits were 1.0 and 0.2 mg kg$^{-1}$ dry soil, respectively. Carbon and particle-size analyses were done by the Colorado State University Soil, Water, and Plant Testing Laboratory. Soil TOC was determined by removing inorganic C and measuring total C remaining by dry combustion (Nelson and Sommers, 1996). Soil CO$_3^2$–C was determined gravimetrically (Soil Survey Staff, 1989). Gravel content was determined by sieving; sand, silt, and clay content were determined by hydrometer (Gee and Bauder, 1986).

A 45 mmol L$^{-1}$ NaOH eluent at 0.3 mL min$^{-1}$ was followed by a 90% acetonitrile (0.3 mL min$^{-1}$) post-column solvent. To account for matrix effects, all samples were spiked with an oxygen-isotope ($^{18}$O)-labeled ClO$_4^-$ internal standard. A 25-μL loop was used for sample loading with a method detection limit of 0.01 μmol L$^{-1}$. The ClO$_4^-$ reporting limit was 0.1 μg kg$^{-1}$ dry soil. Chloride and NO$_3^-$ were analyzed following USEPA Method 845; middle, 845 < Z ≤ 848; upper, 848 < Z ≤ 851.

Table 1. General surface characteristics of local-scale sampling areas used to evaluate distribution differences in shallow-soil (0–30 cm) perchlorate with respect to shrub proximity in three geomorphic settings.

<table>
<thead>
<tr>
<th>Geomorphic setting</th>
<th>Slope gradient</th>
<th>Soil interspace pavement and shallow profile description</th>
<th>Soil carbonate stage†</th>
<th>Geomorphic surface age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoulder slope</td>
<td>2°</td>
<td>well-developed pavement with embedded clasts; vesicular A horizon underlain by dense caliche</td>
<td>IV</td>
<td>Plio-Pleistocene</td>
</tr>
<tr>
<td>Footslope</td>
<td>1°</td>
<td>poorly developed pavement with free-lying clasts; reworked sand with little horizionation, little caliche at depth</td>
<td>I</td>
<td>Holocene</td>
</tr>
<tr>
<td>Valley floor</td>
<td>&lt;1°</td>
<td>well-developed pavement with embedded clasts; vesicular A and thin B horizons, little caliche at depth</td>
<td>I to II</td>
<td>Pleistocene</td>
</tr>
</tbody>
</table>

† Soil carbonate stage and geomorphic surface age from Swedale and Parrish (1988). Stages represent the morphogenetic sequence of soil carbonate accumulation that increases with surface age and range from stage I (youngest surface) to IV (oldest surface) (Gile et al., 1966).
The statistical analysis for determining the effects of geomorphic setting and shrub proximity on shallow-soil ClO₃⁻ and related properties was a 3 × 2 factorial (three settings; two proximities) with four sample replications. For Cl⁻ and NO₃⁻–N values below the reporting level, one half the reporting level was assigned before statistical analyses. This approach is considered acceptable because such values made up <10% of the observations (Lubin et al., 2004). All statistical analyses were done using SAS version 9.2 (SAS Institute, 2008). Analysis of variance, GLM procedure (Steel and Torrie, 1980; SAS Institute, 2008) was used to test main factor (setting and proximity) and interaction (setting × proximity) effects. Before applying ANOVA procedures, residual analyses were used to test assumptions of normally distributed and homogeneous errors and to determine the need for data transformation. The Shapiro-Wilk W statistic was used to test the assumption of normally distributed experimental errors, and residual plots were used to test error homogeneity (Fernandez, 1992). For variables that failed to meet these assumptions, log(x + 1) and square root transformations were evaluated; in all cases the log(x + 1) transformation produced a normal error distribution and more homogeneous errors. The 0.05 probability level was used for ANOVA testing of main factor and interaction effects. Means were compared using Fisher’s protected least significant difference test at the 0.05 probability level (Steel and Torrie, 1980).

Hillslope-scale Distribution of Soil and Plant perchlorate

A grid-based soil and plant sampling approach and detailed topographic survey were combined to evaluate soil, plant, and terrain influences on the distribution of shallow-soil and creosote bush leaf ClO₃⁻ across a representative hillslope (Fig. 2). Soil samples were collected at grid points (n = 49) spaced at 50-m intervals, and, at alternating grid points, a sample of leaves was collected from the nearest creosote bush (n = 25). Creosote bush was selected because it is the most abundant shrub of North American warm deserts (Smith et al., 1997). The radial extent of creosote bush roots can exceed 4 m (Gile et al., 1998). Rooting depth generally corresponds to the maximum annual penetration depth of precipitation, which is influenced by edaphic factors such as soil texture and caliche layers. Soil sampling methods, measured properties, and laboratory analyses were as described above. Leaf samples were collected by clipping and composting three or four foliated stems (~15-cm long) from randomly selected outer branches. Leaves were removed in the laboratory and analyzed for ClO₃⁻ and Cl⁻ concentrations at Texas Tech University. Leaves were extracted according to Rao et al. (2010). Briefly, ~1 g of oven-dried leaves and 25 mL of DIW were placed in a capped centrifuge tube and heated in a water bath for 1 h. Samples were then centrifuged, and 2 mL of supernatant was transferred to a plastic bottle containing activated alumina. The alumina extract mixture was diluted with 18 mL of DIW, capped, and refrigerated for 8 h. The suspension was centrifuged, and the final supernatant was filtered through an activated divinylbenzene resin cartridge. The extraction procedure was repeated for the extraction duplicate, spike, and blank. The solutions thus obtained were analyzed for ClO₃⁻ and Cl⁻ using the procedures previously described for soil analyses. The reporting limits for leaf ClO₃⁻ and Cl⁻ were 100 μg kg⁻¹ and 100 mg kg⁻¹ dry leaf, respectively.

Plant metrics were determined in association with each soil and creosote bush sample. For the soil samples, five metrics were determined for the nearest shrub: height, canopy area, distance to canopy, distance to center, and normalized distance to center (distance divided by canopy radius). For the creosote bush samples, two sampled plant metrics were determined: height and canopy area. Canopy area was calculated as an ellipse using maximum and orthogonal width measurements.

Soil and creosote bush sample points were referenced (northing, easting, and elevation [Z]), and topographic data were collected using a Global Navigation Satellite System—Real Time Kinematic survey with a dual-frequency Ashtech Z-Xtreme receiver (Magellan Corp.). The surveyed area included 150-m-wide buffers surrounding the sampling area. A digital elevation model (DEM) was created, and terrain attributes were calculated using ArcGIS tools (ESRI, 2011). Elevation data were randomly assigned to analysis (n = 45,585) and validation (n = 8699) subsets (Beyer, 2004). The DEM (1 × 1 m cells) used the Hutchinson et al. (2009) interpolation method. The DEM and validation data set elevations were found to be in good agreement (r² > 0.99). Five terrain attributes were derived for each cell (Jeness, 2011): slope gradient (G, degrees), slope aspect (A, degrees), profile or downslope curvature (PROF, radians m⁻¹), plan or across-slope curvature (PLAN, radians m⁻¹), and general curvature (GEN, radians, m⁻¹). Calculations were done according to: G and A (Sharponack and Akin, 1969), PLAN and PROF (Evans, 1979) as modified by Florinsky (1998), and GEN (Moore et al., 1991). Each soil and creosote bush sample point was assigned its measured elevation (Zs and Zc, respectively), and other terrain-attribute values were calculated as the mean of cells within a 5-m radius of the sample point. The 5-m radius was assumed to adequately represent elevation features in the patchy shrub-interspace landscape.

Hillslope soil, plant, and terrain data were evaluated using three types of statistical analyses. First, hillslope segment effects on soil and creosote bush variables were assessed by assigning each soil and creosote bush sample point to one of three elevation-based segments (Fig. 2) and performing a single-factor ANOVA. Residual analysis and data transformation procedures followed those described previously, and single-factor means were compared using Fisher’s protected least significant difference test. The second set of statistical analyses evaluated the direction and intensity of the association between individual pairs of variables using Pearson correlation analysis (Steel and Torrie, 1980). Pairwise analyses for each of the shallow-soil anion (ClO₃⁻, Cl⁻, NO₃⁻–N) concentrations included (i) six soil properties (gravel, sand, silt, clay, TOC, and CO₂–C), (ii) five nearest shrub metrics (height, canopy area, distance to canopy, distance to center, and normalized distance to center), and (iii) six soil pit–centered terrain attributes (Zs, Gs, As, PROFs, PLANs, and GENs). Pairwise analyses for each of the creosote bush anion (ClO₃⁻, Cl⁻) concentrations included (i) the same six soil properties, (ii) two sampled plant metrics (height and canopy area), and (iii) six creosote bush–centered terrain attributes (Zc, Gc, Ac, PROFc, PLANc, and GENc). The third set of statistical analyses used variable-selection regression techniques to quantitatively explore the relative importance of soil, plant, and terrain variables with respect to their influence on the hillslope distribution of shallow-soil anion and creosote bush
anion concentrations. The explanatory variables investigated individually and in combination in the regression analyses were the same soil properties, plant metrics, and terrain attributes as those in the correlation analyses (i.e., a total of 17 and 14 explanatory variables were evaluated in the soil and creosote bush regression analyses, respectively). The all-possible models method R-SQUARE (SAS Institute, 2008) was used to identify optimum candidate models for all subset sizes (one, two, three,... p explanatory variables) where variables contributed directly in an additive manner (i.e., linear model). The Mallows’ C(p) statistic was used to guide the selection of models that were stable and properly specified (i.e., models that did not contain too few or too many variables). Selected candidate models then were evaluated for full model and individual coefficient significance, verification of regression assumptions, multicollinearity among explanatory variables, and potential outliers and influential observations. One soil sample was identified as an outlier and insufficient material was available for reanalysis, so that sample was not included in the hillslope data analyses (Fig. 2). The final optimum subset regression models included only explanatory variables significant at the 0.05 level.

**Atmospheric Deposition**

Atmospheric (wet plus dry, including dust) deposition was assessed over a 6-yr period at the ADRS weather station to characterize the concentration and flux of ClO\textsuperscript{4}\textsuperscript{−} to the valley floor and to assess the magnitude of the direct atmospheric input with respect to the soil and plant reservoirs and cycling. The monitoring period included 2.7 yr before and 3.3 yr after soil and plant sampling. Composite samples collected at approximately quarterly intervals were analyzed for ClO\textsuperscript{4}\textsuperscript{−}, and subsets were analyzed for Cl\textsuperscript{−} and NO\textsubscript{2}\textsuperscript{−}–N. Two funnel–bottle collectors located 1 m apart provided replicate samples. The top of each screened, stainless-steel funnel (98-mm i.d.) was 1 m above land surface; copper tubing connected the funnel to a 1-L glass sample bottle held in an insulated, belowground storage container. Bottles contained a 2-cm layer of mineral oil to prevent sample evaporation. At the end of each collection period, sample bottles were retrieved and replaced by pre-weighed sample bottles (with oil). Retrieved bottles were weighed and kept refrigerated before subsampling for chemical analyses. Subsamples (15 mL) collected from below the oil layer using a disposable plastic pipette were filtered (G × F/0.45 μm nylon membrane, glass fiber prefiltre; Acrodisc) to remove residual oil and debris and placed into a plastic bottle. Sample periods with <1.31 mm of precipitation produced insufficient volume for analysis (<10 mL). Samples of sufficient volume were analyzed for ClO\textsuperscript{4}\textsuperscript{−}, Cl\textsuperscript{−}, and NO\textsubscript{3}\textsuperscript{−}–N using the previously described procedures.

**Isotopic Composition of Nitrate in Soil and Atmospheric Deposition**

Subsets of shallow soil extract solutions and atmospheric deposition samples were analyzed for N and O stable-isotope ratios in NO\textsubscript{3}\textsuperscript{−} to aid evaluation of potential atmospheric and biogenic sources and cycling of NO\textsubscript{3}\textsuperscript{−} in relation to ClO\textsuperscript{4}\textsuperscript{−}. Isotopic analyses were done at the USGS Stable Isotope Laboratory using the bacterial reduction method with *Pseudomonas aureofaciens* (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004), and the data were calibrated by analyzing NO\textsubscript{3}\textsuperscript{−} isotopic reference materials (Böhlke et al., 2003). This method yields accurate δ\textsubscript{15}N values for [NO\textsubscript{3}\textsuperscript{−} + NO\textsubscript{2}\textsuperscript{−}]; however, in soil extracts with low NO\textsubscript{3}\textsuperscript{−} concentrations, the presence of NO\textsubscript{2}\textsuperscript{−} could cause analytical bias in the determination of δ\textsuperscript{18}O (Casciotti et al., 2007). To assess this effect, samples were analyzed by the bacterial reduction method with *Stenotrophomonas nitritireducens*, which is selective for NO\textsubscript{2}\textsuperscript{−} (Böhlke et al., 2007). The NO\textsubscript{3}\textsuperscript{−} concentrations generally were too low for isotopic analysis, but some samples had NO\textsubscript{3}\textsuperscript{−}/NO\textsubscript{2}\textsuperscript{−} ratios high enough (>0.03) to affect significantly the *P. aureofaciens* results for δ\textsuperscript{18}O. For those samples, δ\textsuperscript{18}O values for [NO\textsubscript{3}\textsuperscript{−} + NO\textsubscript{2}\textsuperscript{−}] were estimated by assuming NO\textsubscript{2}\textsuperscript{−} was in isotopic equilibrium with H\textsubscript{2}O (Casciotti et al., 2007), as it was in samples for which such data were available.

**Results and Discussion**

Analytical and statistical results pertaining to soil, plant, and terrain effects on ClO\textsuperscript{4}\textsuperscript{−} distribution in the landscape are summarized in Tables 2–7 and Fig. 3–5. Conceptual models illustrating some of the interactive factors and processes described in the discussion are shown in Fig. 6.

**Local-scale Distribution of Soil Perchlorate in Three Geomorphic Settings**

A feature-based sampling approach was used to investigate the local-scale distribution differences in shallow soil (0–30 cm) ClO\textsuperscript{4}\textsuperscript{−} with respect to shrub proximity within and among geomorphic settings, wherein collocated measurements of relevant soil properties were used to aid interpretation of the ClO\textsuperscript{4}\textsuperscript{−} data. The descriptive statistics and ANOVA results (Table 2) and the geomorphic setting × shrub proximity interaction means (Fig. 3) for each soil property are summarized first to provide context for the subsequent discussion, which uses the full set of results to evaluate factors and processes that affected the soil ClO\textsuperscript{4}\textsuperscript{−} distributions.

Mean soil ClO\textsuperscript{4}\textsuperscript{−} concentrations ranged from 0.3 to 5.0 μg kg\textsuperscript{−}1, and the significant ANOVA setting × proximity interaction (Table 2) showed that the shrub proximity effect varied among settings. For example, VF ClO\textsuperscript{4}\textsuperscript{−} decreased significantly near shrubs, but the FS showed the opposite result (Fig. 3A). Because of the significant interaction, a total of nine pairwise means comparisons are possible (Fig. 3A): one within each of the three geomorphic settings and three within each of the two shrub proximities. Within settings, the means comparison showed a significant 17-fold decrease near shrubs for VF, a significant twofold increase near shrubs for FS, and no significant difference between Far and Near for SS. Within proximities, the means comparisons showed VF significantly greater than FS and SS by a factor of ~2.5 for Far, and VF significantly less than FS and SS by factors of 15 and 10, respectively, for Near. Compared with previous studies, the soil–ClO\textsuperscript{4}\textsuperscript{−} concentrations in Table 2 were much less than those for shallow (0–30 cm) ultraxerous Antarctic soils (31–630 μg kg\textsuperscript{−}1) (Kounaves et al., 2010) but generally greater than those for deep (0.8–13.5 m) unsaturated-zone sediments in the Amargosa Desert (0.1–1.9 μg kg\textsuperscript{−}1) (Rao et al., 2007).
Table 2. Local-scale distribution differences in shallow-soil (0–30 cm) perchlorate and relevant variables with respect to shrub proximity (far and near) within and among three geomorphic settings (shoulder slope, footslope, and valley floor).†

<table>
<thead>
<tr>
<th>Proximity</th>
<th>Source of variation</th>
<th>Particle size‡</th>
<th>TOC§</th>
<th>CO₂–C</th>
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<td></td>
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<td>Si</td>
<td>Cl</td>
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<td></td>
<td></td>
<td>Clay</td>
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<tr>
<td>Far</td>
<td></td>
<td>Gravel</td>
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</table>

Mean soil Cl⁻ concentrations ranged from 1.3 to 137.0 mg kg⁻¹, and those for NO₃⁻–N ranged from 0.3 to 50.4 mg kg⁻¹ (Table 2). Like soil ClO₄⁻, the ANOVA interactions for Cl⁻ and NO₃⁻–N (Table 2) showed that the shrub-proximity effect varied among settings, but means comparisons showed that the proximity differences were not always consistent among the three anions (Fig. 3A–3C). For example, the VF showed a consistent near-shrub decrease for all three anions, but the FS and SS differences varied in terms of significance or general direction.

Mean soil Cl⁻/ClO₄⁻ molar ratios ranged from 3300 to 84,300, and those for NO₃⁻/ClO₄⁻ ranged from 1100 to 73,600 (Table 2). The Cl⁻/ClO₄⁻ ANOVA interaction was outside the prescribed 0.05 significance level, but the main effects of geomorphic setting and shrub proximity were significant (Table 2). As a result, paired comparisons were made using mean values calculated by averaging across the other factor for a total of four possible comparisons (Fig. 3D): three among setting averages and one between proximity averages. Setting-average Cl⁻/ClO₄⁻ molar ratios decreased significantly in the order VF (50,600) > SS (10,350) > FS (3650); proximity averages decreased significantly from Far (34,200) to Near (8830). The NO₃⁻/ClO₄⁻ ANOVA interaction was significant (Table 2), and means comparisons within settings showed an eightfold decrease near shrubs for VF, a sixfold decrease near shrubs for SS, and no significant difference for FS (Fig. 3E). Within proximities, the means comparisons showed VF > SS > FS for Far, and VF > SS ~ FS for Near (Fig. 3E).

The ANOVAs for soil particle-size components showed a significant geomorphic setting effect for gravel, sand, and silt; for clay, no source of variation was significant (Table 2). The FS’s greater sand content (Fig. 3G) corresponded with its profile description and younger surface (Table 1). Greater gravel and silt for the SS and VF (Fig. 3F and 3H) were consistent with their older surfaces, but discrete-depth features such as desert pavement and vesicular horizons (Table 1) were not captured by the 0- to 30-cm depth composite samples.

Soil TOC means ranged from 0.97 to 1.97 g kg⁻¹, and those for CO₂–C ranged from 1.71 to 8.89 g kg⁻¹ (Table 2). Relatively large variability within the TOC data (coefficient of variation [CV] typically ~65–80%) contributed to the lack of significant ANOVA effects (Table 2). The general trends of increasing TOC near shrubs (Fig. 3J), however, were consistent with the “fertile island” structure of desert surface soils whereby organic matter increases near plants due to local organic matter production and interplay to near-shrub transport of litter by wind or water (Anderson et al., 2002; Ravi et al., 2007). The CO₂–C ANOVA showed a significant interaction (Table 2), which is illustrated by the significant near-shrub decrease for the VF versus the opposite trend for the SS and FS (Fig. 3K). The large CO₂–C difference within the VF setting is associated with long-term pedogenesis of the interspace vesicular horizon, which increases CO₂–C retention (Anderson et al., 2002), versus shorter-term bioturbation near shrubs, which disrupts horizon development, increases percolation, and limits CO₂–C accumulation. The SS’s elevated CO₂–C reflects the prevalence of dense caliche at shallow depths (Table 1), whereas the FS’s relatively high values may be linked to the sampling areas’ topographic position on the windward side of the knoll (Fig. 2), which can enhance the accumulation of dust (Hirmas and Graham, 2011) that includes CO₂ fractions (Reheis, 2006).

Results in Table 2 and Fig. 3A through 3E show that geomorphic setting, shrub proximity, and/or their interaction can strongly influence shallow-soil ClO₄⁻ and its relation with other anions. Correlation between soil anion concentrations is...
often used as a general indicator of common depositional sources and evapoconcentration pathways. For example, Antarctic ultraxerous soil (0–30 cm) samples showed high-intensity relations between ClO$_4^-$ and other anions (Cl$^-$, $r \geq 0.97$; NO$_3^-$, $r \geq 0.91$) that were attributed to common atmospheric deposition of all three anions and hyperarid conditions that resulted in no anion transformation in or transport out of the soil (Kounaves et al., 2010). Our geomorphic setting–shrub proximity soil samples showed weaker associations between ClO$_4^-$ and the other anions (Cl$^-$, $r = 0.57$, $p > |r| < 0.01$; NO$_3^-$, $r = 0.60$, $p > |r| < 0.01$ [n = 24]), indicating increased complexity of processes influencing anion distributions in the desert-shrub landscape.

Fig. 3. Local-scale means comparisons for shallow-soil (0–30 cm) variables with respect to shrub proximity in three geomorphic settings: (A) perchlorate (ClO$_4^-$); (B) chloride (Cl$^-$); (C) nitrate as N (NO$_3^-$–N); (D–E) Cl$^-$/ClO$_4^-$ and NO$_3^-$/ClO$_4^-$ molar ratios; (F–I) gravel, sand, silt, and clay contents; (J) total organic carbon (TOC); and (K) carbonate C (CO$_3^-$–C). For significant ANOVA interactions (Table 2), paired comparisons used the S × P LSD test (0.05 level); for significant main effects, averages were compared using S or P LSD (0.05 level).
However, Table 2 and Fig. 3 clearly show that significant portions of the total variation in soil ClO$_4^-$ concentrations are due to geomorphic setting and shrub proximity effects. The following discussion addresses how the collocated soil chemical and physical property data provide insight into the underlying factors affecting the local-scale ClO$_4^-$ distributions within and among geomorphic settings.

For the VF setting, soil ClO$_4^-$, Cl$^-$, NO$_3^-$, N, and CO$_3^-$C concentrations decreased substantially from interspace to near-shrub soil (Table 2; Fig. 3A–3C and 3K). This distribution of constituents in the relatively flat VF setting (<1° slope) (Table 1) reflects soil property and hydrologic influences that contribute to shallow accumulation beneath the well-developed interspace pavement and enhanced leaching near shrubs. In addition to pavement clasts that armor the interspace surface, the underlying silt-rich vesicular A horizon limits infiltration and leaching (Young et al., 2004), so anions that do move into the soil are more likely to be retained. Low infiltration also promotes episodic runoff and anion transport to adjacent near-shrub soil, where increased saturated hydraulic conductivity (Bedford and Small, 2008; Caldwell et al., 2012) enhances localized infiltration and leaching from run-on and direct precipitation. The VF concentration distributions for ClO$_4^-$ and other constituents are generally consistent with the Graham et al. (2008) conceptual model of local-scale, near-surface hydrologic controls on NO$_3^-$ distribution patterns in areas with desert pavement. However, the VF’s large near-shrub decreases for both molar ratios (fivetwofold for Cl$^-$/ClO$_4^-$; eightfold for NO$_3^-$/ClO$_4^-$) indicate that the soil becomes enriched in ClO$_4^-$ relative to the other anions in the vicinity of plants (Table 2; Fig. 3D and 3E). A primary process for soil ClO$_4^-$ enrichment is hypothesized to be a soil–plant cycling input of ClO$_4^-$ from leaf litter. This process is explored further in the sections that follow, but general support for a local-scale increase in leaf-litter near shrubs is suggested by the soil TOC trends (Fig. 3J).

The SS setting also had a well-developed interspace pavement like the VF (Table 1), but SS soil–ClO$_4^-$ concentrations indicated less interspace accumulation and near-shrub leaching (Fig. 3A). Relative to the VF, the SS has a combination of soil and topographic features that could contribute to these reductions. The SS’s prevalence of dense caliche at shallow depth (Table 1; Fig. 3K) should reduce ClO$_4^-$ translocation into the interspace soil and leaching out of the near-shrub soil. The greater slope (2° vs. <1°) and topographic position of the SS sampling areas (Fig. 2) could also reduce local-scale ClO$_4^-$ inputs to the soil due to losses by runoff or wind. Despite these differences between the VF and SS settings, the SS also showed near-shrub decreases for molar ratios (twofold for Cl$^-$/ClO$_4^-$; sixfold for NO$_3^-$/ClO$_4^-$) (Table 2; Fig. 3D and 3E), consistent with local soil–ClO$_4^-$ enrichment from organic matter (Fig. 3J).

In contrast with the other two geomorphic settings, the FS showed a significant near-shrub increase in soil–ClO$_4^-$ concentration (Fig. 3A) and reductions in the magnitude of molar ratios and the associated shrub-proximity differences (Table 2; Fig. 3D and 3E). The molar ratio results indicate that local-scale soil–ClO$_4^-$ enrichment for the FS setting was generally greater and more homogeneously distributed between the interspace and near-shrub soils. Assuming leaf litter contributes to soil–ClO$_4^-$ enrichment, the FS’s more homogenous soil surface (no well-developed pavement; Table 1) with high infiltrability (high sand and low silt contents; Fig. 3F–3H) would allow for more uniform and relatively “unimpeded” translocation of leaf litter ClO$_4^-$ into the shallow soil.

The feature-based sampling results presented above show how the local-scale distribution of soil ClO$_4^-$ varies with respect to shrub proximity within and among geomorphic settings. The data also indicate the occurrence of shallow soil ClO$_4^-$ enrichment, which is hypothesized to result from a leaf litter ClO$_4^-$ input to the soil. This process is further investigated below.

### Hillslope-scale Distribution of Soil and Plant Perchlorate

A grid-based sampling approach and detailed topographic survey were combined to evaluate soil, plant, and terrain influences on the distribution of shallow-soil and creosote bush leaf ClO$_4^-$ across a 9-ha hillslope area (Fig. 2). The discussion that follows addresses the results of three data analysis components that are presented in the order: elevation-based hillslope-segment effects, correlation analysis of the full (nonsegmented) data set, and multiple-regression analyses to quantitatively explore the relative importance of physical and biological factors that influenced the ClO$_4^-$ distributions.

Descriptive statistics, ANOVA results, and means comparisons for evaluating hillslope-segment effects on soil and creosote bush variables are given in Tables 3 and 4. The soil–ClO$_4^-$ concentration for the lower segment was significantly greatest, and the relative ranking of mean values increased in downslope order (Table 3). Soil Cl$^-$/ClO$_4^-$ molar ratios decreased significantly in downslope order, and soil NO$_3^-$/ClO$_4^-$ ratios followed the same trend. These results indicated progressive downslope soil–ClO$_4^-$ enrichment. The leaf–ClO$_4^-$ concentration results (Table 4) followed those for the soil. Although the hillslope-segment effect on leaf–Cl$^-$/ClO$_4^-$ molar ratios was not significant at the prescribed level, the lower-segment ratio suggested leaf–ClO$_4^-$ enrichment roughly twice that of the upslope segments. Results for sand, silt, and clay were consistent with soil- and leaf ClO$_4^-$ results in that the lower segment differed significantly from the other segments (Table 3). The general downslope decrease in gravel and the increase in sand and decreases in silt and clay for the lower-slope segment are consistent with progressive sorting and redistribution by sheet wash acting over geomorphic timeframes. General trends for soil–CO$_3^-$C and sampled plant-metric means point to greater caliche accumulation and poorer growth conditions across the higher hillslope elevations. These results indicate that a variety of interacting factors likely influence ClO$_4^-$ distribution.

The results in Tables 3 and 4 suggest a strikingly high level of ClO$_4^-$ bioaccumulation and selective ClO$_4^-$ uptake by desert shrubs. Leaf ClO$_4^-$ concentrations and leaf–Cl$^-$/ClO$_4^-$ molar ratios on average were ~8000 times greater and 40 times less, respectively, than shallow-soil values. Selective uptake of ClO$_4^-$ relative to Cl$^-$ is indicated by the low leaf–Cl$^-$/ClO$_4^-$ molar ratios across the range of topographic, soil, and plant conditions. In contrast, the leaf Cl$^-$ concentrations did not vary significantly (Table 4) and were similar to the typical crop Cl$^-$ value (1000 mg kg$^{-1}$) needed to meet the micronutrient requirement for chlorine (Marschner, 1995). Our assessment of bioaccumulation and selective uptake is considered qualitative because the soil data do not directly encompass complete root zone--soil
anion concentrations (i.e., the shallow soil samples are “point 0- to 30-cm depth” measurements, whereas leaf measurements represent integrated samples from the relatively large soil volume exploited by plant roots). The high level of natural ClO$_4^-$ uptake by creosote bush at ambient environmental levels is underscored by leaf ClO$_4^-$ concentrations (Table 4) ~10 times those reported for vegetation collected at two highly contaminated sites (Smith et al., 2004; Tan et al., 2004).

The second set of hillslope-scale analyses used the full data set to evaluate the direction and intensity of associations between soil or creosote bush anion concentrations and other soil, plant, and terrain variables (Tables 5 and 6). Soil ClO$_4^-$ concentration showed significant inverse relations with three terrain attributes—elevation (Zs), gradient (Gs), and aspect (As) (Table 5). The strongest association was with Zs, and this inverse elevation relation was consistent with the trend indicated by the hillslope-segment analysis. The Gs relation indicated a slope–gradient effect whereby soils on steeper slopes accumulate less ClO$_4^-$. As discussed below, the correlation results also indicate a concomitant effect of slope aspect on plant growth and leaf ClO$_4^-$ input to the soil. The grid-based analysis did not identify any association between soil ClO$_4^-$ and shrub proximity metrics (Table 5). Unlike the local-scale experiment, wherein near-shrub soil samples were within 1.4 times the canopy radius, the grid samples were collected at an average of 4.0 times the canopy radius. Soil Cl$^-$ showed no significant association with any of the measured variables (Table 5). Soil NO$_3^-$–N showed significant associations with three terrain attributes (Gs, As, and profile curvature [PROFs]), but these relations were directionally opposite and inconsistent with those for soil ClO$_4^-$ (Table 5). Thus, Table 5 shows that the individual factors and/or their level of control on the hillslope distributions were not equivalent among the three anions. However, simple pairwise comparison of soil–ClO$_4^-$ and Cl$^-$ concentrations indicated general co-occurrence ($r = 0.54; P > |r| < 0.01 \ [n = 48]$), but the ClO$_4^-$ and NO$_3^-$ comparison did not ($r = 0.06; P > |r| = 0.66 \ [n = 48]$).

Creosote bush leaf ClO$_4^-$ concentration showed significant associations with three variables (sampled plant height, elevation [Zc], and aspect [Ac]), and leaf Cl$^-$ was associated with two variables (sampled plant height and canopy area) (Table 6). For leaf ClO$_4^-$, inverse relations with elevation and aspect were consistent with those for soil ClO$_4^-$, but the slope-gradient (Gs) relation fell outside the critical region ($P > |r| = 0.07$). The inverse relation between leaf ClO$_4^-$ and aspect may reflect physiological temperature acclimation of creosote bush, which allows it to maintain metabolic activity and growth throughout the year (Smith et al., 1997). Aspect for sampled shrubs decreased from north-northwesterly (336°) to southerly (178°); more southerly aspects would lead to increased winter growth and to the opportunity for concomitant leaf ClO$_4^-$ accumulation.

### Table 3. Hillslope-segment effects on shallow-soil (0–30 cm) variables.†

| Segment† | ClO$_4^-$ | Cl$^-$ | NO$_3^-$–N | Cl$^-$/ClO$_4^-$ | NO$_3^-$/ClO$_4^-$ | Particle size§ | TOC¶ | CO$_2$-C
|-----------|----------|--------|------------|-----------------|-----------------|----------------|-------|--------
| Gravel    | Sand     | Silt   | Clay       |                 |                 | % of total      | % < 2 mm | g kg$^{-1}$ |
| Upper (n = 11) | 1.6 b (0.6) | 0.19 (0.1) | 0.48 (0.3) | 0.84 (0.5) | 0.06 (0.0) | 29.3a (15.4) | 72.4b (5.6) | 13.3a (5.6) | 14.3a (1.9) | 2.39a (1.70) | 9.69a (5.62) |
| Middle (n = 22) | 2.5 b (1.4) | 0.20 (0.1) | 0.73 (0.4) | 1.47 (0.8) | 0.17 (0.1) | 26.4a (13.1) | 72.2b (5.1) | 13.7a (5.2) | 14.1a (1.8) | 1.10b (1.06) | 7.40a (2.60) |
| Lower (n = 15) | 4.9 a (3.7) | 0.20 (0.1) | 0.78 (0.4) | 1.64 (0.8) | 0.21 (0.1) | 20.5a (4.1) | 78.2a (4.9) | 13.5a (4.3) | 12.5b (1.4) | 1.91a (1.35) | 5.96a (0.97) |
| ANOVA Probability†† | 0.001‡‡ | 0.728‡‡ | 0.049‡‡ | <0.001 | <0.001† | 0.309‡‡ | 0.003 | 0.033 | 0.010‡‡ | 0.017‡‡ | 0.091‡‡ |

† Mean and SD (in parentheses) calculated from $n$ observations. Values reported on dry-soil mass basis.
‡ Each sample point assigned one of three segments based on its land-surface elevation (Fig. 2).
§ Particle size categories: gravel >2 mm diam; sand, 0.05–0.1 mm; silt, 0.002–0.01 mm; clay, <0.002 mm.
¶ Total organic carbon.
# Column values followed by the same letter are not significantly different at the 0.05 probability level, as determined by Fisher’s LSD test.
†† Denotes probability that no differences exist within a column; 0.05 probability level used for testing significance of segment effect.
‡‡ Log$_e$(x+1) transformation applied before ANOVA.

### Table 4. Hillslope-segment effects on creosote bush variables.†

<table>
<thead>
<tr>
<th>Segment†</th>
<th>Leaf§</th>
<th>Sampled plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO$_4^-$</td>
<td>Cl$^-$</td>
<td>Cl$^-$/ClO$_4^-$</td>
</tr>
<tr>
<td>µg kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>mol mol$^{-1}$</td>
</tr>
<tr>
<td>Upper (n = 6)</td>
<td>17,400b (5,590)</td>
<td>800a (360)</td>
</tr>
<tr>
<td>Middle (n = 12)</td>
<td>19,600b (6,600)</td>
<td>900a (170)</td>
</tr>
<tr>
<td>Lower (n = 7)</td>
<td>38,800a (11,500)</td>
<td>1100a (520)</td>
</tr>
<tr>
<td>ANOVA Probability#</td>
<td>&lt;0.001††</td>
<td>0.334</td>
</tr>
</tbody>
</table>

† Mean and SD (in parentheses) calculated from $n$ observations.
‡ Each sample point assigned one of three segments based on its land-surface elevation (Fig. 2).
§ Values reported on dry-leaf mass basis.
¶ Column values followed by the same letter are not significantly different at the 0.05 probability level, as determined by Fisher’s LSD test.
# Denotes probability that no differences exist within a column; 0.05 probability level used for testing significance of segment effect.
†† Log$_e$(x+1) transformation applied before ANOVA.
Table 5. Correlation coefficients for determining hillslope-scale associations between shallow-soil (0–30 cm) anion ( perchlorate, chloride, and nitrate as nitrogen) concentrations and other variables (soil properties, nearest shrub metrics, and terrain attributes).

<table>
<thead>
<tr>
<th>Soil anion</th>
<th>Soil property†</th>
<th>Nearest shrub metric</th>
<th>Terrain attribute§</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravel Sand Silt Clay TOC CO$_3$–C Height</td>
<td>Canopy area Distance to Canopy Zs</td>
<td>GS Gs As PROFs PLANs GENs</td>
</tr>
<tr>
<td>ClO$_4$–N</td>
<td>−0.10 0.16 −0.12 −0.17 0.17 −0.14</td>
<td>0.17 0.09 0.11 0.16 −0.07</td>
<td>−0.60* −0.44* −0.32* −0.15 −0.15 −0.15</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.22 −0.08 0.08 0.02 0.13 0.16</td>
<td>0.09 0.00 −0.18 −0.11 −0.14</td>
<td>0.03 −0.01 −0.03 −0.01 −0.07 −0.04</td>
</tr>
<tr>
<td>NO$_3$–N</td>
<td>0.20 −0.20 0.15 0.22 −0.05 0.18</td>
<td>0.16 0.21 −0.14 0.02 −0.17</td>
<td>0.22 0.31* 0.29* 0.27* 0.23 0.26</td>
</tr>
</tbody>
</table>

* Significant at the 0.05 probability level.
† Gravel, >2 mm diam.; sand, 0.05–2 mm; silt, 0.002–0.05 mm; clay, <0.002 mm; TOC, total organic carbon.
‡ Distance from soil sample to center of nearest shrub or shrub clump divided by canopy radius of that shrub or shrub clump.
§ Soil pit–centered attributes are As, slope aspect; GENs, general curvature (concave negative); GS, slope gradient; PLANs, across-slope curvature (concave negative); PROFs, downslope curvature (concave negative); Zs, elevation.

Table 6. Correlation coefficients for determining hillslope-scale associations between creosote bush leaf anion ( perchlorate and chloride) concentrations and other variables (soil properties, sampled plant metrics, and terrain attributes).

<table>
<thead>
<tr>
<th>Leaf anion</th>
<th>Soil property†</th>
<th>Sampled plant metric</th>
<th>Terrain attribute‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravel Sand Silt Clay TOC CO$_3$–C Height</td>
<td>Canopy area Zc Gc Ac PROFc PLANc GENc</td>
<td></td>
</tr>
<tr>
<td>ClO$_4$–N</td>
<td>−0.16 0.28 −0.18 −0.39 0.29 −0.36</td>
<td>0.42* 0.30 −0.72* −0.36 −0.48* −0.26 −0.21 −0.25</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.21 0.33 −0.24 −0.38 0.11 0.18</td>
<td>0.61* 0.45* −0.33 −0.20 −0.30 −0.09 −0.28 −0.19</td>
<td></td>
</tr>
</tbody>
</table>

* Significant at the 0.05 probability level.
† Gravel, >2 mm diam.; sand, 0.05–2 mm; silt, 0.002–0.05 mm; clay, <0.002 mm; TOC, total organic carbon.
‡ Creosote bush–centered attributes are Ac, slope aspect; Gc, slope gradient; GENc, general curvature (concave negative); PLANc, across-slope curvature (concave negative); PROFc, downslope curvature (concave negative); Zc, elevation.

This possibility is supported by a positive association between sampled plant height and leaf ClO$_4$–N (Table 6). Increased height also indicates increased root development in areas of increased water and nutrient availability. For leaf Cl$^-$ concentration, sampled plant height and canopy area showed significant positive relations (Table 6), presumably reflecting the same processes. With the exception of sampled plant height, no variables were significantly associated with leaf ClO$_4$–N and Cl$^-$ concentrations (Table 6). A pairwise evaluation of the hillslope leaf ClO$_4$–N and Cl$^-$ concentrations indicated a marginal relation that fell outside the critical region ($r = 0.36, P > |r| = 0.07 \left[n = 25\right]$).

The third set of hillslope-scale analyses used variable selection regression techniques to explore the relative importance of soil, plant, and terrain variables with respect to their individual and additive influence on the hillslope ClO$_4$–N concentration distributions (Table 7). Complementary analyses of soil Cl$^-$ and NO$_3$–N concentrations were used to assess potential commonality in influential factors. The optimum regression model for soil ClO$_4$–N included two significant, independent, and additive variables and explained 42% of the total variation in hillslope concentrations (Table 7). The two variables were the terrain attributes Zs and Gs, wherein Zs explained 36% of the variation. The negative sign of the Zs and Gs coefficients imply increasing soil ClO$_4$–N with decreasing elevation and slope steepness. Both of these variables are suggestive of processes affecting hillslope deposition and transport of ClO$_4$–N by wind or water. The hillslope distribution of soil Cl$^-$ was not described by any of the variables studied (Table 7). The optimum model for soil NO$_3$–N included one variable, Gs, and explained only 10% of the total variation in hillslope concentrations (Table 7). Although Gs was included in the soil ClO$_4$–N and soil NO$_3$–N regression equations, the coefficients show the direction of the slope–gradient effect was opposite for the two anions. Extreme variability in the distribution of NO$_3$–N in Mojave Desert soils at

Table 7. Optimum regression models for describing the hillslope-scale distribution of shallow-soil (0–30 cm) anion ( perchlorate, chloride, and nitrate as nitrogen) concentrations and creosote-bush leaf anion ( perchlorate and chloride) concentrations.†

<table>
<thead>
<tr>
<th>Regression equation (significance level of individual coefficient)</th>
<th>Soil anion response variable (n = 48)§</th>
<th>Creosote-bush leaf anion response variable (n = 25)¶</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$ or $r^2$</td>
<td>SE</td>
</tr>
<tr>
<td>ClO$_4$–N</td>
<td>484 (&lt;0.001)</td>
<td>−0.57 Zs (&lt;0.001)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>No model with explanatory variables significant at the $P = 0.05$ level</td>
<td>0.059</td>
</tr>
<tr>
<td>NO$_3$–N</td>
<td>0.18 (0.524)</td>
<td>+ 0.39 Gs (0.034)</td>
</tr>
<tr>
<td></td>
<td>2.5 × 10$^4$ (&lt;0.001)</td>
<td>−2888 Zc (&lt;0.001)</td>
</tr>
<tr>
<td></td>
<td>−65.47 (0.813)</td>
<td>+ 1195 Hc (0.001)</td>
</tr>
</tbody>
</table>

† Explanatory variables retained in a given model are significant at the 0.05 probability level.
‡ Significant level of overall model.
§ Soil pit–centered terrain attributes are Zs, elevation and Gs, slope gradient.
¶ Creosote bush–centered terrain attributes are Zc, elevation and Ac, slope aspect; soil properties are CO$_3$–C, carbonate carbon and TOC, total organic carbon; sampled plant metric is Hc, creosote-bush height.
the local interspace and canopy scale has long been recognized (e.g., Hunter et al., 1982; Ewing et al., 2007) and likely affected the quantitative identification of influential factors at the hillslope scale. Within the limitations of the available data, however, the regression results showed a lack of equivalency among the influential variables for soil ClO$_4^-$ and the other anions.

The optimum regression model for leaf ClO$_4^-$ included four variables and explained 74% of the total variation in hillslope concentrations, whereas the model for leaf Cl$^-$ included only one variable (plant height [Hc]) and explained 38% of the total variation (Table 7). The four variables for leaf ClO$_4^-$ were Zc, CO$_3^-$, Ca, and Ac. Separately, Zc explained 52% of the variation; the combination of Zc and CO$_3^-$ explained 61%; and the combination of Zc, CO$_3^-$, Ca, and TOC explained 68%. The negative sign of the Zc coefficient indicates increasing leaf ClO$_4^-$ with decreasing elevation, again reflecting a topographic influence on hillslope deposition and transport processes. The negative coefficient for soil CO$_3^-$ identified a subsurface influence wherein leaf ClO$_4^-$ increases with decreasing presence of caliche in the shallow soil. Caliche can impede ClO$_4^-$ translocation into the soil profile as well as the depth and volume of root development, all of which reduce plant uptake. The positive soil--TOC coefficient indicates increasing leaf ClO$_4^-$ with increasing soil organic matter and presumably reflects spatial differences in soil--plant cycling of ClO$_4^-$. The negative Ac coefficient indicates increasing leaf ClO$_4^-$ with decreasing aspect and, as described previously, may be attributed to a relation between shrub growth and bioaccumulation.

A comparison of the optimum soil--ClO$_4^-$ and leaf--ClO$_4^-$ models (Table 7) shows similarities and differences that, when taken together, provide complementary information about the interacting topographic, edaphic, and biologic controls on the hillslope distribution and cycling of ClO$_4^-$. For example, the soil and leaf models identified elevation as the primary control on ClO$_4^-$, which suggests a strong topographic influence on the hillslope distribution and redistribution of various ClO$_4^-$ inputs to the soil that can include wet and dry atmospheric deposition, eolian dust, and leaf litter. Dust deposition monitoring in the southwestern United States has shown that dust includes organic matter (Reheis, 2003). Thus, topographic effects on the deposition of potentially ClO$_4^-$--enriched dust from outside the grid-sampling area could also contribute to hillslope variations in the available mass and cycling of ClO$_4^-$. After elevation, the influential variables for the two models differed, but these differences were not surprising because the soil--ClO$_4^-$ response variable was measured as a small-volume “point” sample, whereas the leaf--ClO$_4^-$ measurement sampled the full soil volume exploited by the shrub root system. Thus, the leaf--ClO$_4^-$ model provides a more comprehensive view of surface and subsurface controls on the distribution and cycling of ClO$_4^-$ across the hillslope.

**Atmospheric Deposition**

Perchlorate concentrations and fluxes in atmospheric (wet plus dry, including dust) deposition were characterized over a 6-yr period, and results are shown in Fig. 4. Precipitation differences between replicate collectors were small (average CV, 2%) (Fig. 4A). Cumulative precipitation totaled 535 mm for the 2207-d monitoring period. This was ~8% less than that obtained at the adjacent (~1 m away) ADRS weather station rain gauge (582 mm) (Johnson et al., 2007; Arthur et al., 2012); the difference may be due in part to under-catch in the deposition collectors, which had a smaller sampling diameter (98 mm) than the standard rain gauge (203 mm). Measureable precipitation fell during 23 of the 25 collection periods, but the volume for one period (~2 mL) was insufficient for chemical analysis. Atmospheric deposition ClO$_4^-$ concentrations for the 22 remaining periods ranged from 74 to 2193 ng L$^{-1}$ and averaged 608 ± 567 (SE) ng L$^{-1}$. Perchlorate concentration correlated inversely with precipitation amount ($r = -0.61; P > |r| < 0.01$). Three of the four highest ClO$_4^-$ concentrations were measured during the April/May to August collection periods, and the fourth was measured during August to November (Fig. 4B). All of these periods had relatively low precipitation (<10 mm) and corresponded with seasonal increases in convective thunderstorms and winds (Arthur et al., 2012), conditions that could increase putative atmospheric and deflationary dust ClO$_4^-$ contributions. Atmospheric deposition of Cl$^-$ and NO$_3^-$--N (data not shown) were determined for a subset of collection
periods. The Cl$^-$ concentrations averaged 1.22 ± 1.16 (SE; n = 15) mg L$^{-1}$ and were significantly correlated with ClO$_2^-$ (r = 0.84; P > |r| < 0.01). The NO$_3^-$--N concentrations averaged 1.66 ± 1.58 mg L$^{-1}$ (SE; n = 21) and correlated with ClO$_2^-$ (r = 0.89; P > |r| < 0.01). The associated molar ratios for Cl$^-$/ClO$_2^-$ averaged 6600 ± 3200 (SE), and NO$_3^-$/ClO$_2^-$ averaged 22,000 ± 9800 (SE).

To our knowledge, only one other study has quantified ClO$_2^-$ concentrations in total atmospheric deposition (i.e., wet plus dry, including dust), and that work was done on Long Island, New York (Munster et al., 2009). The ADRS ClO$_2^-$ concentrations were within the range of Long Island values, where artificially high values (up to 2780 ng L$^{-1}$) were attributed to fireworks displays. Even so, the ADRS average was ~3 times that for Long Island (210 ng L$^{-1}$), suggesting the importance of dry deposition in addition to the factor of 10 difference in annual precipitation. In comparison to southwestern wet deposition—only results (Rajagopalan et al., 2009), the average ADRS atmospheric deposition ClO$_2^-$ concentration was ~38 times that for wet deposition (16.1 ng L$^{-1}$), and the Cl$^-$/ClO$_2^-$ molar ratio was one third that for wet deposition (18,200).

The ClO$_2^-$ atmospheric deposition flux for the 22 analyzed periods ranged from 0.20 to 3.16 mg ha$^{-1}$ d$^{-1}$ (Fig. 4C). The difference between calculated fluxes for the replicate collectors was small (CV <20% for most periods) and was attributed more to variability in measured concentrations than to variability in measured precipitation amounts (Fig. 4). Collection-period flux magnitudes were marginally correlated with precipitation amount (r = 0.38; P > |r| = 0.08) and were not correlated with ClO$_2^-$ concentration (r = 0.08; P > |r| = 0.73). The cumulative atmospheric deposition flux was 1815 mg ha$^{-1}$ for periods with analyzed samples (1932 d total), which equates to an annual flux of 343 mg ha$^{-1}$ yr$^{-1}$. The Munster et al. (2009) deposition study did not assess fluxes, but Rajagopalan et al. (2009) reported that the average ClO$_2^-$ wet deposition flux for southwestern sites was 36.0 mg ha$^{-1}$ yr$^{-1}$, which is an order of magnitude less than the ADRS total atmospheric deposition flux. It is not possible to determine the specific wet deposition and dry deposition (colian dust, atmospheric aerosols, and gases) contributions to total deposition with our present data set, but the relative concentration and flux comparisons noted above strongly indicate that dry deposition is an important contributor of ClO$_2^-$ in desert environments. Dust accumulation monitoring in the Great Basin and Mojave Desert has shown that colian dust fluxes are substantial, ranging from 20 to 200 kg ha$^{-1}$ yr$^{-1}$ (Reheis, 2006). Further study of dry deposition components with long-term monitoring is needed to better understand their contribution to total atmospheric ClO$_2^-$ deposition.

**Atmospheric Deposition in Relation to Soil and Plant Perchlorate Reservoirs and Cycling**

An atmospheric source and precipitation vector to the soil have been strongly implicated for naturally occurring ClO$_2^-$ in unsaturated zones and groundwater of the southwestern United States (e.g., Dasgupta et al., 2005; Plummer et al., 2006; Rajagopalan et al., 2006; Rao et al., 2007; Jackson et al., 2010), but the importance of plant-recycled inputs versus direct atmospheric inputs has not previously been recognized. The present study has identified the potentially important role of selective plant uptake, foliar concentration, and leaf-drop return to the soil surface that results in recycling and concentration of ClO$_2^-$ in the soil. A comprehensive evaluation of the direct atmospheric versus leaf-cycled ClO$_2^-$ inputs is beyond the scope of this study, but estimates of soil and plant ClO$_2^-$ reservoirs and analysis of data that include limited but instructive values of NO$_3^-$ stable isotope ratios provide support for the posited plant cycling effects.

Scoping calculations were performed to assess the relative magnitude of the atmospheric deposition ClO$_2^-$ flux (343 mg ha$^{-1}$ yr$^{-1}$) with respect to area-weighted estimates of ClO$_2^-$ reservoirs in shallow soil and creosote bush leaves. Using the weighted average hillslope soil ClO$_2^-$ concentration (3.0 µg kg$^{-1}$) (Table 3) and a bulk density of 1.61 Mg m$^{-3}$ (Andraski, 1996), the shallow-soil ClO$_2^-$ reservoir is 14,490 mg ha$^{-1}$. This value is ~40 times the annual atmospheric deposition ClO$_2^-$ flux, suggesting a 40-yr accumulation time if direct atmospheric deposition is the only input to the 0- to 30-cm soil zone and if losses are negligible. However, based on multiple-year field and modeling studies of soil water movement at the ADRS where the root zone is ~0.75 to 1 m deep (Andraski, 1997; Garcia et al., 2011), four decades without ClO$_2^-$ loss is highly unlikely because percolation and plant water uptake from the upper 30 cm of soil occur commonly during normal and above-average precipitation conditions. Thus, the sizeable shallow-soil ClO$_2^-$ reservoir cannot result solely from direct atmospheric deposition alone and must be supplemented by plant cycled/recycled inputs to the soil surface. To estimate the leaf ClO$_2^-$ reservoir, the weighted average hillslope creosote bush leaf concentration (24,400 µg kg$^{-1}$) (Table 4) was combined with average creosote bush community data collected on the valley floor during the springs of 2006 to 2011 (ground cover, 5.1%; canopy area, 0.78 m$^2$ shrub$^{-1}$; line-transect method [Smith, 1974]) and a canopy-area based estimate of leaf biomass (Ludwig et al., 1975). The resultant mass of ClO$_2^-$ in the standing crop of leaves is 1310 mg ha$^{-1}$. This mass is approximately 4 times the annual atmospheric flux and one tenth the shallow-soil mass, and it represents an aboveground reservoir from which accumulated ClO$_2^-$ may be released when plant and climatic conditions are conducive to leaf drop. For creosote bush, partial and episodic releases are likely because it is a drought-resistant evergreen that can retain leaves through extended drought periods (Smith et al., 1997). As an illustrative example, a 25% per annum leaf drop would approximately equal the annual atmospheric flux. The shallow-soil and leaf ClO$_2^-$ reservoirs estimated above are based on representative concentrations measured at a single point in time, but spatial and temporal heterogeneities in these reservoirs can be caused by dynamic plant uptake and release processes and by episodic percolation events that transfer ClO$_2^-$ out of the root zone soil and into the underlying unsaturated zone sediments.

Relative comparisons of chemical and isotopic data support the leaf-cycled ClO$_2^-$ input hypothesis. For example, in the lower-slope segment of the hillside where topographic, soil, and plant features were most conducive to enhanced ClO$_2^-$ cycling, the average Cl$^-$/ClO$_2^-$ molar ratio for soil was 2800 (Table 3), compared with 6600 for atmospheric deposition and 80 for leaves (Table 4), suggesting soil enrichment by ClO$_2^-$ release.
from plants. The NO$_3^-$/ClO$_4^-$ molar ratios for lower-slope segment soil (1100) (Table 3) and total deposition (22,000) could also be consistent with leaf-induced soil ClO$_4^-$ enrichment, but this comparison is less straightforward because NO$_3^-$ can be influenced by several N cycling processes. Evidence for such processes may be reflected in the isotopic composition of NO$_3^-$ in arid region soils (e.g., McMahon and Böhlke, 2006; Ewing et al., 2007). In the present study, NO$_3^-$ stable isotope composition was determined for subsets of atmospheric deposition samples ($n = 6$) and local-scale shallow-soil samples (Fig. 5). Atmospheric deposition δ$^{15}$N averaged $-0.7 \pm 1.6\%_o$, and δ$^{18}$O averaged $+70.8 \pm 3.7\%_o$. Soil δ$^{18}$O means comparisons indicate the mixing of atmospheric (high δ$^{18}$O) and biogenic (low δ$^{18}$O) NO$_3^-$ varied among geomorphic settings and between shrub proximities, and these results were consistent with anticipated variations in leaf ClO$_4^-$ inputs to the soil. For example, lower δ$^{18}$O[NO$_3^-$] main-effect averages for footslope and near-shrub soils (+12.0 to +13.7‰) (Fig. 5B) indicate a greater biogenic source influence where conditions are conducive to greater cycling and release of leaf ClO$_4^-$ to the soil. In contrast, elevated δ$^{18}$O[NO$_3^-$] main-effect averages for the valley floor, shoulder slope, and far-from-shrub soil (+19.4 to +21.3‰) (Fig. 5B) indicate a smaller biogenic source influence where desert pavement and/or distance from shrubs presumably contribute to a reduction in the amount of leaf litter available for release of ClO$_4^-$ into the soil. Generally, lower soil δ$^{15}$N[NO$_3^-$] values far from shrubs in the FS and SS settings could be consistent with less N cycling in less biologically active locations (Fig. 5A). Greater soil δ$^{15}$N[NO$_3^-$] far from shrubs in the VF setting, however, might result from relatively large amounts of NO$_3^-$ reduction or microbial uptake where surface features were more favorable for intermittent wetting and moisture retention (flat, paved, silt-rich soil [Table 1]).

These relative comparisons are incomplete and uncertain, but they provide additional support for the development of the conceptual diagrams shown in Fig. 6. These simplified, two-dimensional diagrams combine results from the local-scale, hillslope-scale, and atmospheric deposition components of this study and illustrate interactive factors and processes influencing the distribution and cycling of ClO$_4^-$.

The apparent importance of leaf ClO$_4^-$ underscores a need for further study of the role of plants in the distribution and seasonal to annual cycling of natural ClO$_4^-$ in desert ecosystems. Seyfferth and Parker (2008) reviewed research on ClO$_4^-$ in plants and noted that several major questions remain about species differences in uptake and accumulation and about the fate of ClO$_4^-$ in abscised leaves. The present study focused on creosote bush, but limited sampling of other species suggested that their leaf ClO$_4^-$ concentrations were of the same order of magnitude as that observed for creosote bush (e.g., shadscale [$n = 2$], 8000–32,000 μg kg$^{-1}$; burrobush [$n = 1$], 19,000 μg kg$^{-1}$). In contrast to creosote bush, drought-deciduous shrubs such as

![Fig. 6](image-url)
burrobush can drop all of their leaves in response to seasonal drought conditions, can produce leaf cohorts in winter and summer, and may achieve higher leaf area per unit biomass than evergreens (Smith et al., 1997). Thus, differences in shrub physiology and phenology may influence the amount and timing of ClO$_4^-$ inputs to the soil, and even the less dominant shrubs could be important if their smaller aerial extent is offset by increased leaf production and frequency of leaf drop.

Results from this study have implications for assessing risks associated with ecological health and with potential mobilization of natural ClO$_4^-$ to groundwater. Direct ingestion of soil by livestock and wildlife (e.g., Mayland et al., 1975; Beyer et al., 1994; Esque and Peters, 1994) and transfer from soil through plants to higher organisms can contribute to ClO$_4^-$ exposure in a desert landscape. The creosote bush canopy represents a previously unrecognized ClO$_4^-$ reservoir (1310 mg ha$^{-1}$). Creosote bush is browsed by many small mammals, and other desert shrubs, including shadscale, burrobush, willowberry, and Mormon tea, are browsed by livestock and wildlife (USDA, 2013). Deep unsaturated-zone ClO$_4^-$ reservoirs have been recognized as a potential threat to groundwater because their mobilization can adversely affect water quality (Rao et al., 2007). Although the ClO$_4^-$ inventory for the shallow soil reported here (14,490 mg ha$^{-1}$; 0–30 cm) is smaller than that reported for an Amargosa Desert deep unsaturated-zone sediment profile (152,000 mg ha$^{-1}$; 0.8–13.5 m) (Rao et al., 2007), the depth-normalized average for shallow soil (48,300 mg ha$^{-1}$ m$^{-1}$) is 4 times that for the deeper profile (11,970 mg ha$^{-1}$ m$^{-1}$).

Conclusions

To our knowledge, this study is the first to characterize the distribution and interactions of natural ClO$_4^-$ in a terrestrial ecosystem. Soil and creosote bush leaf ClO$_4^-$ concentrations were influenced by topographic, soil, and plant effects on deposition, transport, and soil–plant cycling. The ClO$_4^-$ cycle is hypothesized to include atmospheric deposition, selective plant uptake, leaf bioaccumulation, and leaf drop to the soil surface that results in soil–ClO$_4^-$ enrichment and recycling. Relative comparisons between measured atmospheric (wet plus dry, including dust) deposition and previously published results indicated that dry deposition is an important contributor of ClO$_4^-$ in deserts. A comparison between the measured atmospheric deposition flux of ClO$_4^-$ and the estimated leaf canopy ClO$_4^-$ identified the canopy as a large and previously unrecognized aboveground reservoir from which ClO$_4^-$ may be released when plant and climatic conditions are conducive to leaf drop.

Future assessments of natural ClO$_4^-$ exposure in desert ecosystems should consider the mass of aboveground and complete belowground reservoirs while accounting for local-scale and larger-scale heterogeneity. Moreover, transient accumulation, redistribution, and loss processes affected by topography–soil–plant–water interactions can influence ClO$_4^-$ cycling and the potential release to deep unsaturated zones and groundwater. Findings of the study have implications beyond natural ClO$_4^-$ because establishment of background levels and better understanding of terrestrial interactions will aid the identification, interpretation, and treatment of anthropogenically contaminated systems.

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